Selective Ring Opening Allene Metathesis: Polymerization or Ruthenium Vinylidene Formation

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ABSTRACT: Selective ring-opening allene metathesis polymerization (ROAlMP) and ruthenium vinylidene formation from 1,2-cyclononadiene (**1**) by simple catalyst selection are discussed. Grubbs second generation catalyst (G2) favors the formation of an alkylidene leading to the ROAlMP of (**1**). Grubbs first generation catalyst (G1) favors vinylidene formation and prevents the homopolymerization of (**1**) even at elevated temperatures. Isolation and characterization of poly(**1**) by NMR analysis and MALDI-TOF confirms the generation of a well-defined polyallene that exhibits good thermal stability (T_D ca. 400 ºC) and fluorescent properties. Ring-opening metathesis polymerization (ROMP) of a high strained norbornene derivative (NBE-^{i}Pr) at 80 ºC using the ruthenium vinylidene generated from (**1**) is also investigated. The discovery of ROAlMP allows for the simple accesses of well-defined polyallenes from commercially available catalysts and will ultimately guide structure-property determinations of polyallenes.

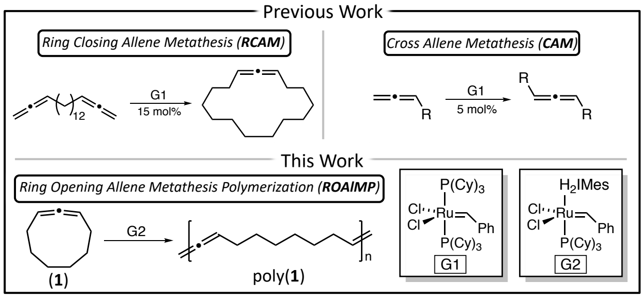
Introduction:

Allenes, the simplest class of cumulenes, were discovered over a century ago.[1] They have become a staple in the modern organic chemists toolbox as a direct result of the myriad of chemical transformations made possible by their unique structure[2,3] and can be found in over 150 natural products, pharmaceuticals[4], and even elastomers.[5] From a materials context, they are known as “carbon-rich, shape-persistent, axially chiral scaffolds”.[6] Yet, their exploration in polymers is limited. The lack of employment of allenes in soft materials chemistry stems from a scarcity of polymerization techniques that preserve the functionality of allenes and as a consequence, the materials produced generally lack functional utility.[7] A handful of reports that successfully incorporate allenes into the repeating structure of a material are known, however, these reports typically require specialized catalyst systems and only produce oligomers.[8-12]

An alternative route to polyallenes was recently demonstrated via post-polymerization transformation.[13] In the report, the authors carried out a two-step Skattebøl rearrangement on *cis*-poly(norbornene) resulting in allene incorporation at varying percentages (20-95%) along the backbone. While this method represents a simplistic general route to polyallenes, it does come with shortcomings as pointed out by the authors. The synthetic methodology relies upon a *cis* olefin geometry that can only be prepared through the use of a specialized *Z*-selective catalyst. On top of this, the incorporation of allenes occur in a random and non-quantitative manner, which may limit its application/scope. A polymerization that retains the allene functionality during the polymerization and utilizes commercially available catalysts is a potentially useful methodology for the generation of polyallenes. A polymerization of this sort would increase the tuneability and accessibility of polyallenes, ultimately allowing for structure-property determinations.

Metathesis based polymerizations that utilize Grubbs catalyst such as ROMP[14] and acyclic diene metathesis polymerization (ADMET)[15], represent two of the most powerful polymerization techniques investigated over the past two decades. This is in part due to the benchtop stability and high functional group tolerance of Grubbs catalyst. With the emergence of alternative metathesis polymerizations such as cyclopolymerizations[16], metallotropy[17], and enyne metathesis polymerizations[18], its surprising that the polymerization of allenes, which are known to be reactive with Grubbs catalyst, remain unexplored.[19]

Scheme 1. Allene Metathesis



The utilization of allenes in metathesis is surprisingly limited (**Scheme 1**). The first documented report on allene metathesis was in 2000 in which terminal mono-substituted allenes underwent cross-allene metathesis (CAM) with Grubbs first generation catalyst (G1).[20] While not all derivatives underwent successful/productive metathesis, this was the first account showing that allenes behave analogously to alkenes in

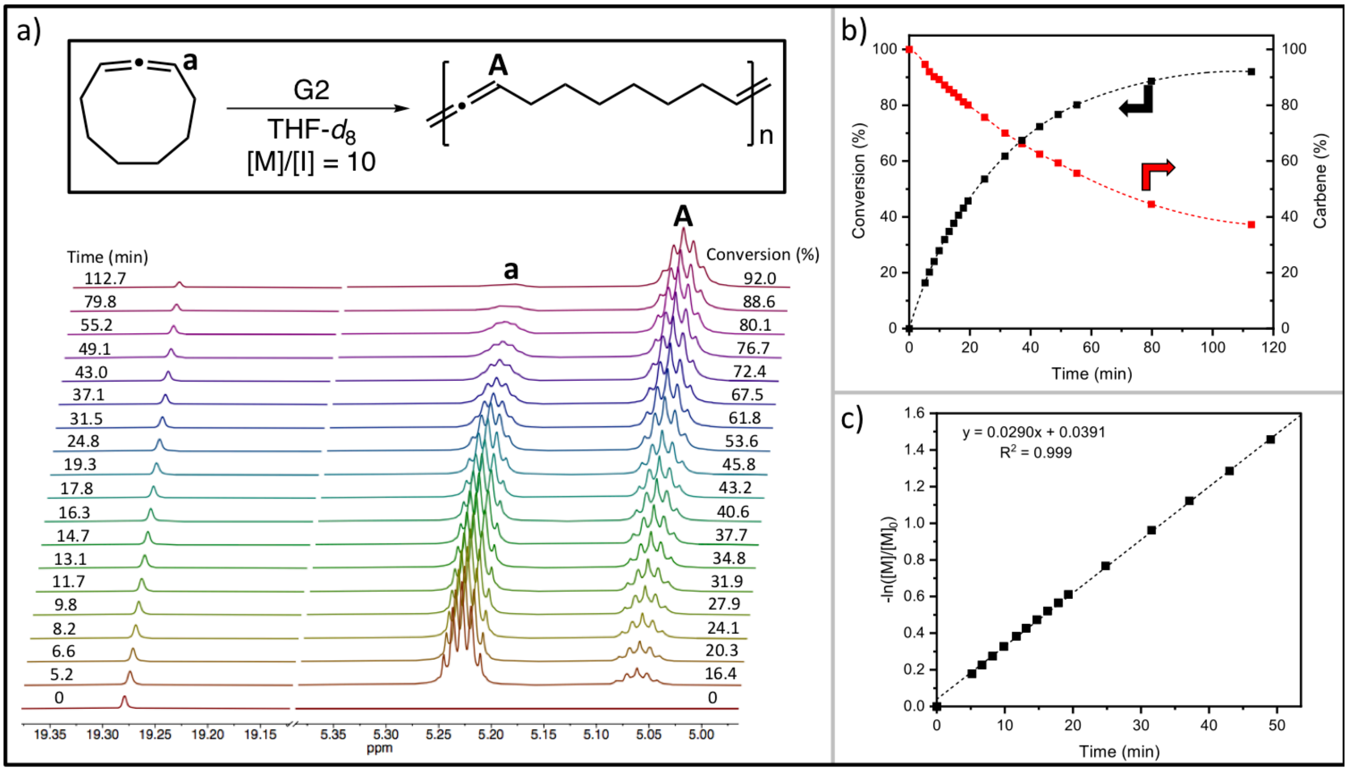


Figure 1. a) Stacked ^{1}H-NMR spectra monitoring the formation of poly(**1**) in THF-d_8 at 25 ºC. b) Residual carbene and polymerization conversion vs. time. c) Linear plot of –ln([M]/[M]$_0$) vs. time showing first order kinetics.

cross metathesis. It was later shown that macrocyclic allenes (n = 15-19) could be accessed by ring closing allene metathesis (RCAM) also utilizing G1, albeit in low yields.[21] These two accounts represent the only reports of allene metathesis with Grubbs catalyst in literature but highlight their potential utility. Despite the dearth of precedent, we hypothesized that the ring-opening metathesis polymerization of cyclic allenes yields polyallenes, analogous to the generation of polyolefins from ROMP. Successful polymerization would allow for the precise installment of allenes into the repeating structure of materials without the use of complex catalyst systems or post-polymerization modifications. Herein, we report the ring opening allene metathesis polymerization (ROAlMP) of a cyclic allene and discuss the general features of this polymerization.

Results and Discussion:

ROMP is driven by the release of ring-strain of its cyclic olefin monomer, so it stands to reason that a similar requirement exists for the opening of cyclic allenes. Unfortunately, unlike strained cyclic alkenes, cyclic allenes (ring size ≤ 8) are thermally unstable and dimerize rapidly under ambient conditions, making them impractical for polymerization.[22] However, it has been shown that medium sized rings (ring size ≥ 9), such as 1,2-cyclononadiene (**1**), are accessible on the gram-scale via the Doering−LaFlamme−Skattebøl rearrangement and are stable under ambient conditions (dimerizing at ca. 100 ºC).[23] Being the smallest thermally stable cyclic allene available, we began by investigating the ring-strain of (**1**) to determine if it was sufficiently strained for polymerization. An isodesmic reaction analysis, analogous to ROMP ring-strain calculations, was used to determine the ring-strain of the system (**Figure S8**).[24] Consistent with a prior report, (**1**) exhibits 12.7 kcal/mol of ring-strain, a value between *cis* and *trans*-cyclononene.[25] Larger rings, such as 1,2-cyclodecadiene were also investigated and showed a comparable ring strain (15.9 kcal/mol). However, for the focus of this report, we set aim on the polymerization of (**1**) due to its facile accessibility in grams scale quantities compared to 1,2-cyclodecadiene.

Initial polymerization investigations of (**1**) were conducted with Grubbs second generation catalyst (G2). As seen in **Figure 1**, at a monomer to initiator ratio ([M]$_0$/[I]$_0$) of 10 with [M]$_0$ = 1 M in THF-d_8 at 25 ºC, a disappearance of the olefinic signal (δ 5.23) and the concomitant appearance of a new upfield peak at δ 5.06 (A) was observed via ^{1}H-NMR. After 2 hours, the material reached 92% conversion with 37% residual carbene (**Figure 1b**). The polymerization showed first-order kinetics with respect to monomer concentration (**Figure 1c**) and exhibited a relatively slow propagation (k_{obs} = 0.0290 min^{-1}). To see if the use of a coordinating solvent had an effect on the polymerization, the polymerization was repeated in toluene-d_8. To our surprise, the polymerization in toluene-d_8 proceeded 3x slower (k_{obs} = 0.0095 min^{-1}) than THF-d_8, leading to lower conversions (60%) over a longer reaction time (2.5 hours) (see **Figures S9-11**). The use of THF as a weakly coordinating ligand has been used advantageously in prior studies to increase the stability of propagating carbenes[26]; however, no indication of a new THF-alkylidene complex was observed and the stability of the carbene was only marginally improved in THF-d_8 compared to toluene-d_8 (81% vs. 75% respectively after ca.17.5 minutes).

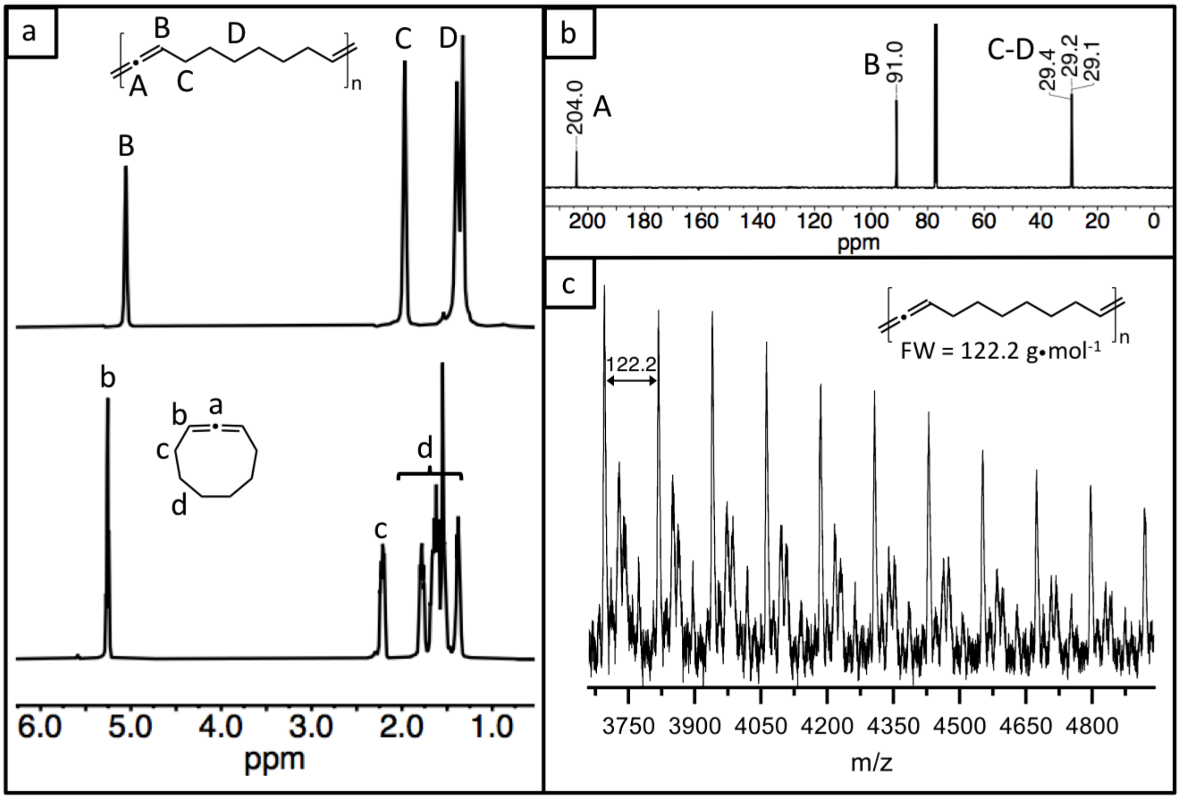


Figure 2. a) Stacked ^{1}H-NMR spectra of (**1**) and poly(**1**) in $CDCl_3$ (25 ºC). b) ^{13}C-NMR of poly(**1**) in $CDCl_3$ (25 ºC). c) MALDI-TOF of poly(**1**) with the correct repeating unit mass observed.

While it seems unlikely that THF is behaving in this manner, due to the improved propagation rates, THF was chosen as our solvent of choice.

Confirmation of the proposed constitutional repeating unit (CRU) of poly(**1**) was obtained by NMR characterization. Poly(**1**) was first isolated by precipitation into cold methanol (-78 ºC) and vacuum dried before characterization. **Figure 2a** shows stacked spectra of the monomer and isolated material in $CDCl_3$. Integrations of the obtained spectra along with COSY correlations match the proposed CRU (**Figure S12-13**). Gratifyingly, ^{13}C-NMR (**Figure 2b**) showed the appearance of the central *sp*-hybridized allene carbon at δ_C 204, slightly upfield from that observed in (**1**) at δ_C 206. MALDI-TOF of a larger isolated poly(**1**) was also conducted to confirm the repeating structure and as can be seen in **Figure 2c**, a repeating structure on average of 122.2 g•mol^{-1} was observed, matching the predicted CRU.

With evidence of a successful homopolymerization via G2, we screened various polymerization conditions, starting with catalyst loadings, and monitored their effect on the polymerization. Catalyst loadings from 4.0-0.5% (($[M]_0/[I]_0$ = 25 – 200) were attempted and had a dramatic effect on the polymerization conversion (**Table 1**). Highest conversions (52.6%) were obtained at high catalyst loadings ($[M]_0/[I]_0 = 25$) whereas only low conversions (10.2%) were obtained at lower loadings ($[M]_0/[I]_0 = 200$). This dependency of catalyst loading is attributed to the instability of the propagating species, resulting in low catalyst turnover.

Initial monomer concentration, which can have large effects depending upon the strain of the monomer, was next ivestigated.[27] Interestingly, conversions were not particularly sensitive to monomer concentrations, as ca. 48% conversion was obtained over the range of concentrations tested (3.0 – 0.5M). However, decreasing concentration did lead to increasing *Đ* (1.89 – 2.78) which is indicative of intrachain backbiting where higher $[M]_0$ help to increase propagation rates relative to backbiting, leading to lower *Đ*.[28]

Lastly, we screened reaction temperatures from 0 – 50 ºC. This range covers conventional reaction temperatures used in ROMP, and is lower than the boiling point of THF. At a constant $[M]_0$ and catalyst loading, the polymerization was highly sensitized to reaction temperatures, with a 50 ºC change leading to a 72% conversion increase. Surprisingly, elevated temperatures led to the highest conversions, contrary to what is commonly observed in most ROMP systems. We hypothesize that elevated temperatures allow the system to combat the slow propagation alongside the relatively unstable propagating species. Although elevated temperatures are generally deleterious to metathesis, serving to shorten catalyst lifetimes while increasing entropic penalties associated with the polymerization[29], they have been successfully employed in systems where increased catalytic activity are needed or slow propagation is observed.[30] At elevated temperatures, increased conversions compared to room temperature trials were obtained (44% vs. 81% at ($[M]_0/[I]_0 = 50$). Molecular weights remained unchanged, likely due to increased chain transfer.

After the screening and optimization of polymerization conditions with G2, we next studied the effects of catalyst structure on polymerization. Differences in Grubbs catalyst structure have interestingly shown selectivity difference towards allenes, alkenes, and alkynes.[19] Second generation catalysts (G2 and Hoveyda-Grubbs second generation (HG2)) show a preference towards alkynes over allenes and alkenes, whereas first generation species (Grubbs first generation (G1) and Hoveyda-Grubbs first generation (HG1)) show a selectivity of allenes over alkenes and alkynes, with G1 showing an order of magnitude higher selectivity of allenes over alkenes. Additionally, the prior CAM and RCAM reports both successfully

Table 1. Screening of Polymerization Conditions for poly(**1**) with G2.

[M]/[I]	$[M]_0$	Temp. (ºC)	Time (h)	Conversion (%)^a	$[M]_{n,Theo.}$ (kDa)^b	M_n (kDa)^c	$Đ^c$
25	3	25	2	52.6	1.6	8.8	2.48
50	3	25	2	44.4	2.7	13.7	1.89
75	3	25	2	24.6	2.3	11.5	1.91
100	3	25	2	17.3	2.1	11.8	1.82
150	3	25	2	13.8	2.5	11.0	1.83
200	3	25	2	10.2	2.5	11.0	1.79
50	2	25	2	48.5	3.0	9.9	2.07
50	1	25	2	51.5	3.1	5.8	2.65
50	0.5	25	2	48.4	3.0	3.8	2.78
50	1	0	3	9.1	0.6	8.3	1.92
50	1	50	1	81.0	4.9	4.6	4.34
100	1	50	1	39.4	4.8	10.8	1.80
250	1	50	1	23.1	7.1	10.1	1.82

$^{a)}$ Conversions determined by ^{1}H-NMR analysis in $CDCl_3$ (25 ºC). $^{b)}$ Determined by ([M]/[I]*conversion)*FW_1. $^{c)}$ Determined by SEC (RI) in THF based off a 12 point conventional column calibration using narrowly dispersed polystyrene standards.

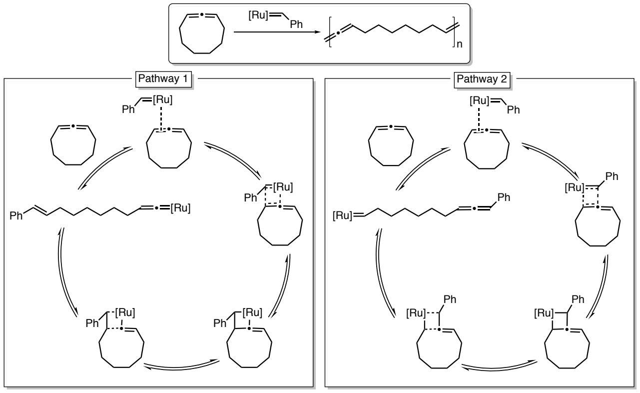
employed G1 as their catalyst choice.

To see if the increased allene selectivity of G1 was beneficial for ROAlMP, (**1**) was subjected to G1 at $[M]_0/[I]_0 = 10$, $[M]_0 = 1$ M in toluene-d_8. Unfortunately, after similar reaction times as G2 trials, no polymerization had occurred. In contrast to G2 trials that showed a slow disappearance of the alkylidene peak with increasing conversions, a complete and rapid disappearance of the alkylidene peak (δ 20.5) occurred in 5 minutes. To understand why G1 was not reactive towards ROAlMP, we investigated the possible mechanistic pathways of the reaction.

Scheme 2 shows the two possible pathways that lead to the same CRU. In pathway 1, the catalyst undergoes 2,1-insertion, leading to the generation of a ruthenium vinylidene as the catalytic species. First generation ruthenium vinylidenes have been generated through multiple synthetic pathways, and show extremely limited reactivity towards metathesis compared to their second-generation counterparts.[31] In pathway 2, 1,2-insertion of the catalyst leads to a standard alkylidene catalytic species. Insight into the mechanistic pathway from previous CAM and RCAM reports were indeterminate (**Figure S23**).

The reaction pathway was elucidated by ^{13}C NMR analysis in comparison to previously reported first generation vinylidene species. As seen in **Figure 3**, ^{13}C NMR spectra of the $[M]_0/[I]_0 = 10$ trials show a clear difference between catalysts. For G2, an alkylidene peak at δ_C 295 was observed as well as both allene peaks from unconsumed monomer and polymer, indicating pathway 2 is dominant for G2. For G1, a new peak at δ 336 ppm was observed, similar to other first generation ruthenium vinylidene species.[32] Further confirmation of a ruthenium vinylidene came from ESI-HRMS of a $[M]_0/[I]_0 = 1$ trial that showed a m/z at 909.4908 (909.4937 calc.) indicative of the $[M-Cl]^{+\bullet}$ commonly observed in the ESI-MS of Grubbs catalyst.[33] This study demonstrated that simple variations of the catalyst structure selectively lead to alternative mechanistic pathways for G1 and G2.

Scheme 2. Mechanistic Pathways of ROAlMP.



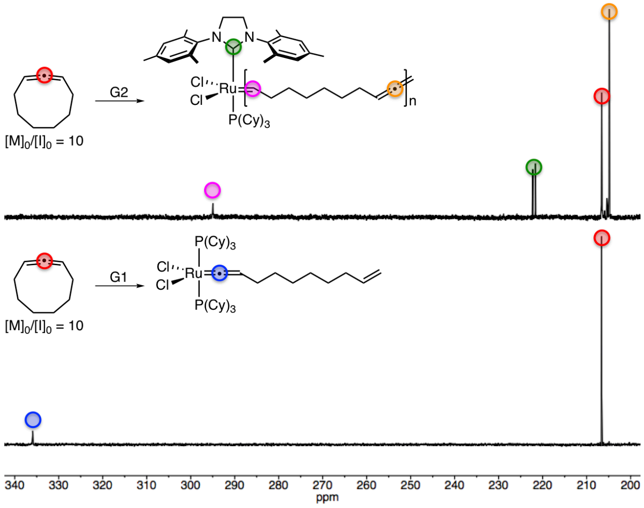


Figure 3. Stacked ^{13}C-NMR spectra in toluene-d_8 (25 ºC) of [M]/[I] = 10 trials of (**1**) with (bottom) G1 and (top) G2.

While G1 led to the formation of a ruthenium vinylidene, this new catalyst species did not result in productive polymerization of (**1**) at room temperature. Given that first generation vinylidenes have shown limited reactivity in olefin metathesis, we hypothesized that elevated temperatures would increase the activity of the ruthenium vinylidene towards ROAlMP. Trials with G1 at $[M]_0/[I]_0 = 10$ were repeated and subsequently heated to 50 ºC upon the complete formation of the vinylidene at room temperature and subsequently monitored via ^{1}H-NMR. Disappearance of monomer over an hour was observed along with the generation two new downfield peaks at δ 5.8 and 5.6. Upon triple precipitation into MeOH at -78 ºC, both downfield peaks disappeared and only aliphatic protons were observed (**Figure S1-2**). No allene signal was observed in ^{13}C-NMR of the isolated material and we are currently unable to assign a correct microstructure for this polymer.

Although the homopolymerization of (**1**) was not viable with G1, we hypothesized that the vinylidene is active towards highly strained species such as norbornene. Generation of the ruthenium vinylidene was repeated, this time with only slight excess of (**1**). Upon complete disappearance the alkylidene signal, 10 equiv of NBE-^{i}Pr was added and monitored via ^{1}H-NMR (**Figure 4**). Unfortunately, no polymerization of NBE-^{i}Pr was observed at room temperature, even after extended reaction times. However, upon heating the reaction mixture to 80 ºC for 2.5 hours, near quantitative conversion to Poly(NBE-^{i}Pr) was obtained. The reformation of an alkylidene was not observed after 2.5 hours which is likely caused by the limited lifetime of the catalyst at elevated temperature.[29] Although this process is not controlled, it serves as a proof of concept that the selective formation of a ruthenium vinylidene from G1 serves to catalyze highly strained systems.

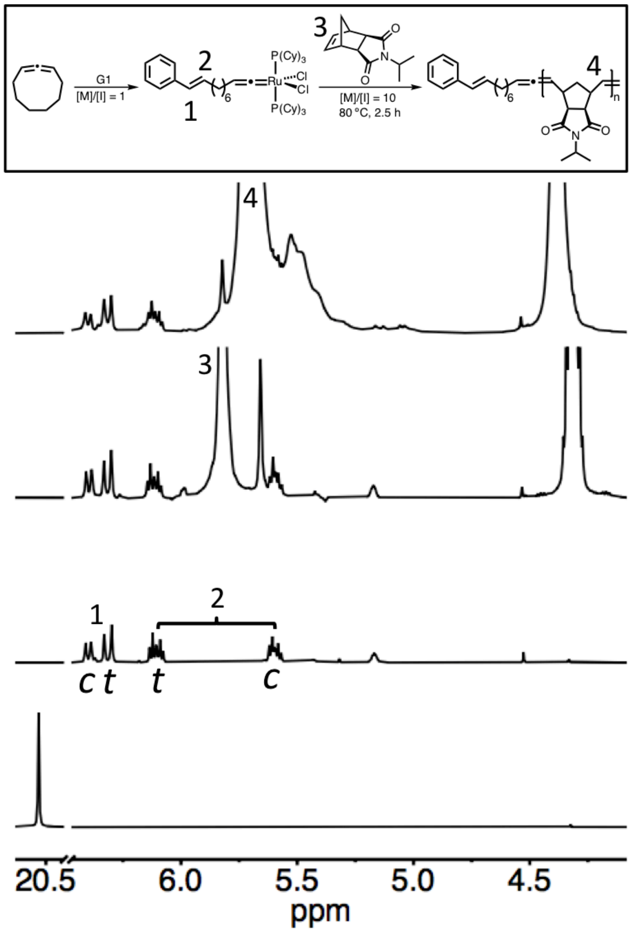


Figure 4. Stacked ^{1}H-NMR spectra in toluene-d_8 of polymerization of NBE-^{i}Pr using a ruthenium vinylidene. (Bottom) G1 at t = 0 min. (Middle bottom) Ruthenium vinylidene. *c* and *t* stand for *cis* and *trans*, respectively. (Middle top) Ruthenium vinylidene and NBE-^{i}Pr at 25 ºC. (Top) Poly(NBE-^{i}Pr) after 2.5 h at 80 ºC with ruthenium vinylidene.

Thermal and photophysical properties of poly(**1**) were also preliminarily investigated. Thermogravimetric analysis (TGA) of the isolated material under nitrogen showed good thermal stability, with 5% mass loss occurring at 400 ºC (**Figure S18**). This value is similar to decomposition temperatures observed for the previously produced polyallene from *cis*-poly(norbornene).[13] Differential scanning calorimetry (DSC) from -60 – 100 ºC at both 10 and 20 ºC•min^{-1} did not show any indication of a glass transition temperature (T_g) (**Figure S19**) even though poly(**1**) shares a similar microstructure to poly(cyclooctene), whose T_g is -60 ºC. Photophysical properties of our poly(**1**) sample were also investigated with both UV-Vis and fluorometry experiments. Similar to prior studies, broad emissions (λ_{EM} = 360-660 nm) at 1.0 mg•mL^{-1} in THF of poly(**1**) were observed, consistent with recently reported allene-containing polymers (**Figure S20**).[13]

Conclusion:

Ring opening allene metathesis of a cyclic allene is reported for the first time using G2. The polymerization exhibited increased conversions at elevated temperatures, catalyst loadings, and when conducted in THF. Spectral characterization confirms the generation of an allene on every 8th carbon backbone, leading to the first well-defined polyallene system. The materials show good thermal stability and are a potentially useful reactive scaffold for post-polymerization modifications in the future. G1 was shown to selectively form a ruthenium vinylidene that exhibited low catalytic activity. Turnover of the species was demonstrated at elevated temperatures with the use of strained cyclic alkenes. Gaining control of the ROAlMP and the vinylidene are important next steps needed to maximize the utility of these methods in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis and characterization of compounds (PDF)

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